

# Simultaneous measurement of volatility of Zr, Hf and Rf

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Rutherfordium belongs to the group-4 elements as Zr and Hf. It is well known that the chemical properties of Zr and Hf very resemble with each other and halides of these elements are volatile. From the relativistic calculations RfCl<sub>4</sub> is predicted to be more volatile than ZrCl<sub>4</sub> or HfCl<sub>4</sub> [1-3], whereas from the extrapolation, exactly the opposite trend is expected [4,5]. In this special case, the predictions about the relative volatility of RfCl<sub>4</sub> compared to ZrCl<sub>4</sub> and HfCl<sub>4</sub> can be directly tested experimentally in a gas phase.

Türler et al. investigated the volatility of the Hf- and Rf- chlorides with OLGA II [6,7]. They showed that the volatility of the chlorides of the group-4 is very similar among them. Later, HEVI system was developed by Kadkhodayan *et al.* [8] and the volatility of the Zr, Hf and Rf chlorides was investigated. The result shows that the order of volatility is RfCl<sub>4</sub> > ZrCl<sub>4</sub> > HfCl<sub>4</sub> [9]. However, each chloride was studied in a separate experiment, so that chemical conditions may have been different among the experiments. And the reported correlation is not consistent that expected from the sublimation enthalpies of Zr and Hf. Türler *et al.* [10] investigated the volatility of the Hf- and Rf- chlorides again, and they showed RfCl<sub>4</sub> > HfCl<sub>4</sub> in volatility but did not discuss about Zr chloride.

In the present work, in order to clarify the above mentioned ambiguity, the investigation for volatility of Zr, Hf and Rf chlorides was performed under the identical conditions.

The isothermal chromatographic apparatus consists of a reaction chamber, an isothermal column, and a re-clustering chamber. Each section is made by quartz and connected in a series. The isothermal column is a spiral tube with the 2000 mm long and 3 mm inner diameter. The reaction chamber and the isothermal column were heated independently up to a maximum temperature of 1200° C by electric furnaces.

In order to investigate the isothermal gas chromatographic behavior of Zr, Hf and Rf in the same condition, an irradiation for the production of Zr, Hf and Rf isotopes were performed at the same time at the JAERI 20-MV Tandem accelerator. A target chamber and an irradiation setup are shown in Fig. 1. <sup>85</sup>Zr was produced by the <sup>nat</sup>Ge(<sup>18</sup>O, xn) reaction. <sup>167,169</sup>Hf were produced by the <sup>152</sup>enriched Gd(<sup>18</sup>O, xn) reaction and <sup>261</sup>Rf was produced by the <sup>248</sup>Cm(<sup>18</sup>O, 5n) reaction.

Produced activity is transported from the target chamber to the gas chemistry apparatus via He/KCl gas-jet transport system. The activity-laden aerosols were transported by the helium through a 2.2 mm i.d. stainless steel tube to the gas chromatography apparatus. The stainless steel capillary was employed in order to eliminate any exchange of oxygen through the capillary walls. The concentration of residual oxygen was monitored with the oxygen monitor and was less than 30 ppm for experiment. Domanov *et al.* observed that in gas chromatography experiments the transportation of Zr and Hf chlorides could not be affected by oxygen in this order of amounts [11]. As a chlorinating agent, a mixture of chlorine gas and carbon tetrachloride vapor was used. Chemical reaction took place in the reaction room at 1000° C. The chemically separated species were attached to new KCl aerosol, and transported for  $\alpha$  measurement to the detection system MANON [12], which is a rotating wheel detection system with a 80 cm $\phi$  wheel, 80 collection positions, and six pairs of Si PIN photodiodes. The activity-laden aerosols were deposited on a

polyethylene terephthalate foil of  $120 \mu\text{g}/\text{cm}^2$  in thickness and 20 mm in diameter. Each sample was collected for 30 s and measured for 180 s.

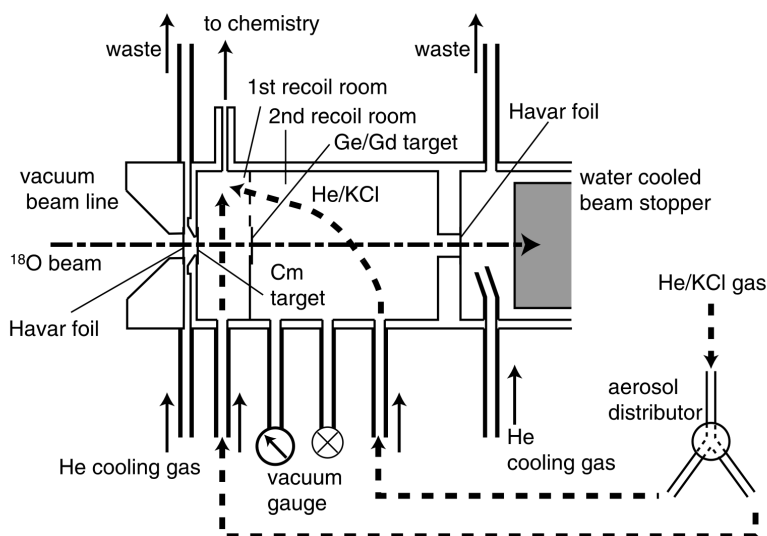


Figure 1. Schematic of the target chamber utilized for simultaneous production of Zr, Hf and Rf isotopes.

The obtained  $\alpha$  spectrum is depicted in Fig. 2. The spectrum is dominated by  $\alpha$ -lines from the contaminants  $^{211}\text{Bi}$  and  $^{211\text{m},212\text{m}}\text{Po}$  which also form volatile chlorides. Due to the much effort to prevent Pb contamination, the level of background  $\alpha$ -particles from them was reduced compared with those by Kadkhodayan *et al* [9]. The  $\alpha$ -particle group of 8.00-8.40 MeV was assigned to  $^{261}\text{Rf}$  ( $T_{1/2}=78$  s) and its daughter  $^{257}\text{No}$  ( $T_{1/2}=26$  s).

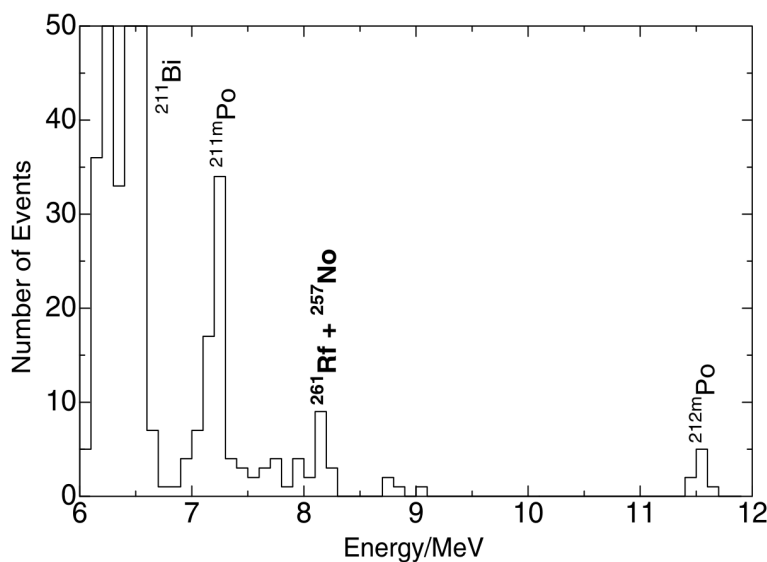


Figure 2.  $\alpha$  spectrum after chemical separation.

In Fig. 3 the measured yields of the 8.00-8.50 MeV  $\alpha$ -particle group, that of the 454 keV ( $^{85}\text{Zr}$ ) and of 493 keV ( $^{169}\text{Hf}$ ) are shown as a function of the temperature of the isothermal column. At the isothermal temperature of 300° C, a part of Zr, Hf and Rf chlorides were transported to the outlet of the isothermal column. The yield of Zr, Hf and Rf chlorides increased rapidly with the increase of the isothermal temperature, and reached the maximum around 350° C. This rapid change of yield with column temperature is characteristic of the simple adsorption-desorption transport mechanism [13]. Furthermore, since oxygen concentration was kept at less than 30 ppm in the system, it was not considered that the oxychlorides would be concerned with chromatographic transportation [11]. Therefore, it was concluded that the volatile compounds of these three elements would be the tetrachlorides and that they would behave very similar to each other.

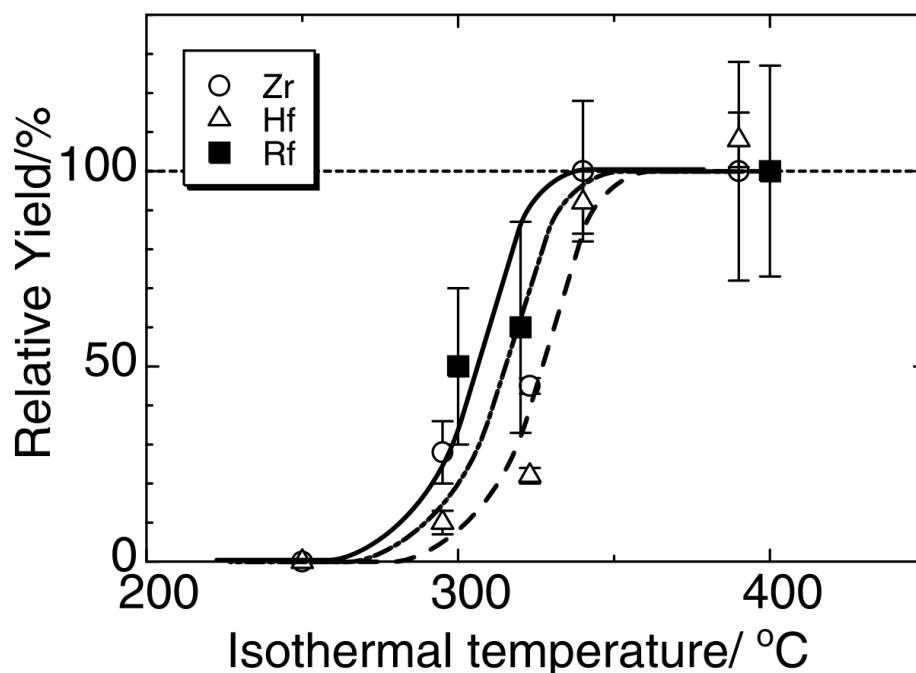


Figure 3. Relative yield curves for  $^{85}\text{Zr}$ -,  $^{167}\text{Hf}$ - and  $^{261}\text{Rf}$ -chlorides. The lines are calculated yield curves from a Monte Carlo simulation.

It should be mentioned that after prolonged gas chemistry experiments in the present work, the quartz surface of the chromatography column is partially coated with a thin layer of KCl, which means that of the chromatography was performed on KCl rather than on  $\text{SiO}_2$ . As a volatility measurement is strongly dependent on the column surface, we cannot directly compare the present results to those of others. However, relative comparison among the elements is supposed to be reasonable. In this work, Zr and Hf were examined simultaneously, and it was found that the volatility of their chlorides was similar with each other. This result agrees with the expectations from macro scale chemistry. Since Rf chlorides behaved similarly with Zr and Hf on this surface, it is expected that Rf chlorides would have similar volatility. An adsorption enthalpy was calculated using a Monte Carlo simulation based on a microscopic model [14-16] and the following adsorption enthalpies for the group-4 chlorides were obtained for partially KCl coated quartz surfaces: Zr:  $-118 \pm 6$  kJ/mol, Hf:  $-116 \pm 6$  kJ/mol and Rf:  $-112 \pm 10$  kJ/mol.  $\text{ZrCl}_4$  and  $\text{HfCl}_4$  were found to have very similar adsorption enthalpies. This tendency is consistent with the results for NaCl surface [17,18].

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